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Dissolved Trace Elements in Lake Biwa

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A clean technique for analysis of freshwater has been developed. Lake water was collected from the northern basin of Lake Biwa, an oxic and monomictic lake, from 21 May 1994 to 4 December 1998. Dissolved trace elements (Al, P, V, Cr, Mn, Fe, Ni, Zn, As, Y, W and U) were measured by high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS). Their spatial and temporal distributions were strongly affected by the cycle of Fe and Mn.

Keywords: dissolved trace elements / freshwater / Lake Biwa /clean technique / HR-ICP-MS

Trace elements in freshwater have been studied with a view to understanding biogeochemical cycles of elements and protecting the environment from pollution. It has become clear that concentrations of dissolved trace elements in freshwater are lower than those previously reported (e.g., Pb and Cd in the Grate Lakes [1]). Contamination with trace elements through sampling, filtration, preconcentration and determination has been a serious problem. Investigation of trace elements in oxic lakes has been difficult, because many elements are present at a low concentration under well-oxygenated conditions. The northern basin of Lake Biwa (Northern Lake) is both a mesotrophic and monomictic lake, of which the water column is enough deep (average 44 m) to develop a summer thermocline but oxic throughout the year. We have developed a clean technique for the determination of trace elements in fresh water and observed their spatial and temporal distributions in Northern Lake. This is one of the largest set of data collected on dissolved trace elements in an oxic lake.

The lake water samples were collected by a Niskin sampling bottle or a Niskin-X sampling bottle, of which inner spring and latex tubing were replaced with silicon tubing. The interior of the samplers was precleaned with a standard procedure, which contains cleaning with detergent and 4 M HCl followed by rinsing with ultra pure water (MQW) produced with a Milli-Q water system. Immediately after sampling, lake water was transferred to a low-density polyethylene (LDPE) bottle using a silicon tubing and bell in order to prevent contamination with airborne particles. The LDPE bottle was precleaned with the standard procedure and with hot 4 M HCl, hot 0.5 M

INTERFACE SCIENCE — Hydrospheric Environment Analysis —

Scope of research

Research activities are concerned with geochemistry, oceanography, limnology and analytical chemistry, which are important basic sciences in order to realize the sustainable society. Major research subjects are as follows: (i) Biogeochemistry of trace elements in the hydrosphere. (ii) Hydrothermal activity and deep biosphere. (iii) Fe-uptake mechanism of phytoplankton. (iv) Ion recognition. (v) Non-linear chemical reaction.

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HNO_3 and hot MQW. The samples were filtered on board with a closed filtering system constructed in a clean box. The closed filtering system was assembled with LDPE bottles, PFA tubing and a PFA filter holder. PFA materials were precleaned by heating in a mixture of H_2SO_4, HNO_3 and $HClO_4$. The interior of the filtering system was cleaned with hot 0.5 M HNO_3 and hot MQW before use. Polycarbonate membrane filters (0.2 μm of pore size) were precleaned by heating in a mixture of acids (1 M HCl, 0.5 M HNO_3 and 0.5 M HF) and in MQW. Using clean N_2 gas pressure, the sample solution was passed through the filter and collected in another LDPE bottle. The sample was acidified to pH 1 with ultra pure HNO_3 for preservation.

Simplifying the analytical procedure is the best way to reduce the risk of contamination. High-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) has the highest sensitivity to analyze simultaneously multi-elements in solution [2]. The method allows one to determine the total concentration of dissolved trace elements in freshwater directly. Dissolved concentrations for Al, P, V, Cr, Mn, Fe, Ni, Zn, As, Y, W and U were determined by a calibration curve method. The accuracy of the HR-ICP-MS measurement was ascertained for Al, V, Cr, Mn, Fe, Ni, Zn, As and U by analysis of a certified riverine water reference material (SLRS-3; National Research Council, Canada). Our results corresponded to the certified values within 10%. The interference from matrices for the 12 elements was studied by analyzing a Lake Biwa water sample with and without spiked elements. The recovery was quantitative for all the elements (93-104%).

In order to estimate a blank value throughout the procedure, MQW was filtrated and acidified on board the ship. The blank represented as the field blank and the detection limit throughout the procedure defined as three times the standard deviation of the field blank are listed in Table 1. The field blank values for Cr, Mn, Fe, Ni and Zn are on the same order of magnitude as with that obtained in the Great Lakes using a portable clean laboratory [1]. The field blank and detection limit values are low enough to allow determination of the 12 elements in the lake water.

The concentration ranges of the trace elements at N1, off Ohmi-maiko (75 m of water depth), are shown in Table 1. The medians of Mn, Fe, Ni, Zn and U found in this study are lower than the minimum concentrations reported previously (7.5, 18, 4.8, 11 and 0.084 nM, respectively [3]). The difference between our data and the previous data may originate from a difference in size fractionation. The previous workers used a filter of 0.4-0.45 μm of pore size. Another possibility is that the data of the previous workers may have been influenced by contamination.

Table 1. Field blank (pM), detection limit (pM) and concentrations at N1 (nM).

Element	Field blank (pM)	Detection limit (pM)	Concentration at N1 (nM)		
			Min.	Max.	Median
Al	687 ± 8	23	1.1	672	29
P	2050 ± 79	236	26	586	82
V	15 ± 3	11	0.79	5.7	2
Cr	15 ± 1	3.6	0.38	5.1	0.83
Mn	146 ± 1	3.6	0.36	311	5.1
Fe	525 ± 9	26	< 0.026	611	12
Ni	29 ± 1	4	1.6	25	3.5
Zn	429 ± 18	54	0.35	68	3.1
As	54 ± 4	12	5.2	25	11
Y	0.57 ± 0.04	0.13	0.049	0.27	0.11
W	0.73 ± 0.01	0.022	0.013	0.13	0.045
U	0.21 ± 0.03	0.076	0.027	0.2	0.061

The feathers of distribution of the dissolved trace elements are following. The residence time of Al, Fe and Mn was the shortest (0.03-0.12 yr) and the particulate/dissolved ratio was as high as 26-45. While the dissolved concentrations of Al, Fe, Mn and Y were uniformly low throughout the water column at N1, maximums occurred occasionally at the surface, thermocline and bottom. These maximums were caused by precipitation, resuspension of sediments and reductive dissolution of Fe and Mn oxides in the anoxic sediments. The concentrations of Cr, Ni and Zn were almost uniform throughout the water column but increases at the surface were sometimes observed. These distributions suggest that the effects of strong scavenging by Fe and Mn oxides prevail over the effects of the biogeochemical cycle and that atmospheric flux is significant for these metals. The concentrations of As and P increased with depth during the stagnation period. Their distribution was controlled by the biological cycle and scavenging of Fe and Mn oxides. The oxyacid species, such as V, W and U, accumulated in the epilimnion and were removed from the bottom during the stagnation period. This behavior may be attributed to the pH dependent interaction of these elements with Fe and Mn oxides.

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